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SITES AND DIFFUSION FOR MUONS AND HYDROGEN IN TITANIUM HYDRIDES

W. J. Kossler[1], H. E. Schone[1], K. Petzinger[1], B. Hitti[1], J. R. Kempton[1], E. F. W. Seymour[2], C. E. Stronach[3], W. F. Lankford[4], and J. J. Reilly[5]

[1] College of William and Mary, Williamsburg, VA 23185 USA
[2] University of Warwick, Coventry CV4 7AL, UK
[3] Virginia State University, Petersburg, VA 23803 USA
[4] George Mason University, Fairfax, VA 22030 USA
[5] Brookhaven National Laboratory, Upton, NY 11973 USA

Low temperature sites for muons implanted in TiH_x have been found to be a mixture of interstitial and substitutional sites, with substitutional occupancy determined by the probability that a muon in an interstitial site will have a vacant nearest neighbor substitutional site. As with ZrH_x, activation from the interstitial site is observed below 300 K. From the depolarization rate in the substitutional site, the muon likely displaces the neighboring H atoms by about 0.1 A. Diffusion for the substitutional muons occurs above room temperature with an activation of about 0.38 eV, which is less than the 0.505 eV for hydrogen vacancy motion observed by NMR. To explain this the muon transition rate to a vacancy must be less than that of hydrogen.

1. Introduction

The study of metal hydride systems with μSR presents an excellent opportunity to observe the interaction between positive muons and hydrogen and their related diffusion and site preference. The present measurements investigate muon diffusion in the γ(fcc) and δ(fct) phases of titanium hydride with varying hydrogen concentration. Titanium hydride is a convenient material for such studies because the moments of the titanium nuclei are very small and thus only μ-H (and H-H) interactions need be considered. Previous studies of other hydrides have shown that the activation energy for a muon at high temperatures need not be equal to the activation energy for a hydrogen atom, and that the muon and hydrogen compete for sites in the host lattice /1,2/. It is seen in figure 1 that the depolarization rate for the three samples studied can be naturally considered in four different regions: I) a low temperature concentration-dependent plateau, II) a transition to a lower rate (motional narrowing) which occurs below room temperature, III) a room temperature, concentration-independent plateau, and IV) a second motional narrowing region due to diffusion of muons and hydrogen on the tetrahedral lattice.

2. Experiment

The transverse field experiments were conducted with the stopping muon beam at Brookhaven National Laboratory /3/. The samples were TiH_x with x=1.99, 1.97, and 1.83. For low temperature measurements, we used a flow cryostat for x=1.99 and a helium Displex closed-cycle refrigerator for the other two samples. Above 300 K, a heated-water circulating system was used for x=1.99, and an oven, consisting of resistive wire wrapped around an aluminum frame, was used for x=1.97 and 1.83. The data were fit on-line to Gaussian curves and off-line to Abragamian forms. The correlation times obtained from the Abragamian form were then fit to an Arrhenius expression to obtain the activation energy E_a.

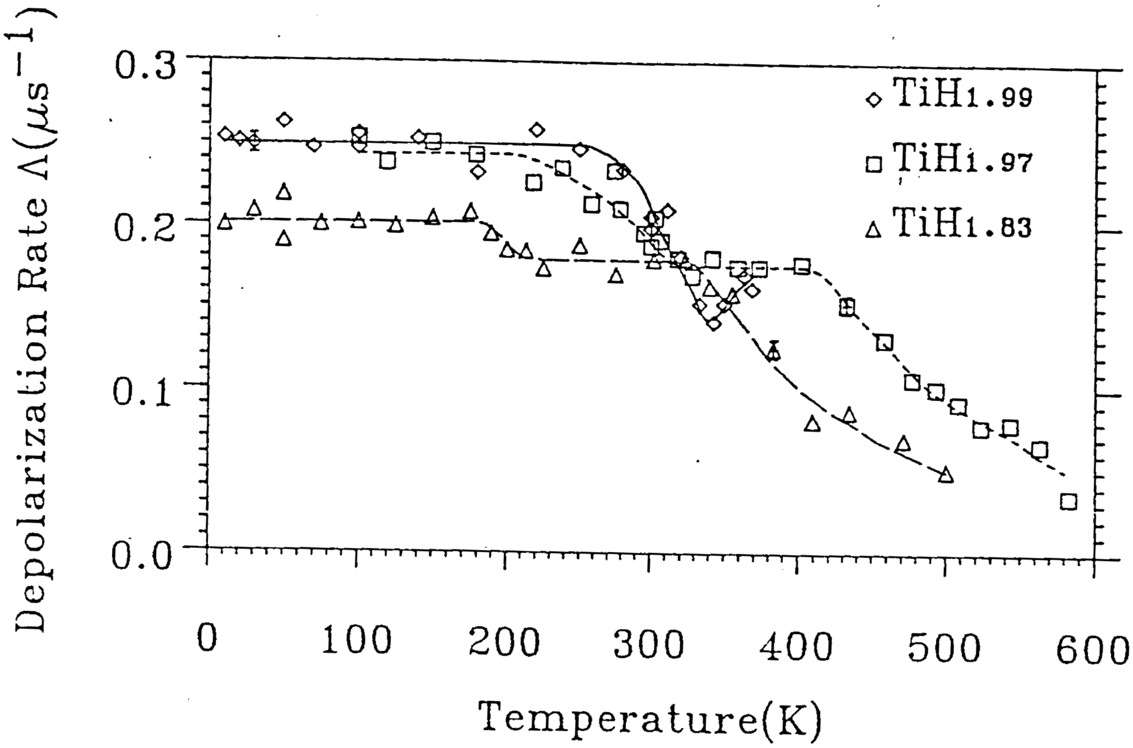

Fig.1. The muon depolarization rate, Λ, as determined from a Gaussian form ($P_x(t)=\exp(\Lambda^2 t^2)$) plotted as a function of temperature for the three samples. The lines in the figure have been added to guide the eye.

3. Results and Discussion

For the case of identical spins in a polycrystalline material the Van Vleck formula /4/ for the second moment is:

$$\Delta^2=(4/15)I(I+1)\gamma_I^2\gamma_\mu^2\hbar^2\sum_i 1/r_i^6 . \tag{1}$$

One can calculate the linewidths for the tetrahedral and octahedral sites since Λ is proportional to the square root of the second moment. The depolarization rate (including hydrogen-hydrogen interactions which reduce Λ by 5% for both sites /5/) for the O site ($\Lambda=0.298\ \mu sec^{-1}$) is much larger than that for the tetrahedral site ($\Lambda=0.189\ \mu sec^{-1}$). This will serve as a guide to distinguish octahedral and tetrahedral site occupancy as we discuss the various regions of the spectra.

3.1. Region I

The spectra for all three samples show that the muon is stationary for low T. It is found that Λ is concentration dependent with the x=1.99 sample having the highest value and the x=1.83 sample the lowest. This indicates that the muon is more likely to find the more slowly depolarizing tetrahedral sites as the hydrogen concentration decreases. Over the low temperature region $\Lambda(T)$ seems to be independent of T. For each sample we then have obtained a Λ_{EXP} which we find can be parameterized by:

$$\Lambda^2_{EXP} = \Lambda^2_{OCT}(1-P) + \Lambda^2_{TET}P, \qquad (2)$$

$$\text{where } P=8(1-x/2). \qquad (3)$$

This parameterization follows from the assumption that the muon stops randomly on octahedral sites first and then, if a nearest neighbor tetrahedral site is vacant, rapidly moves to that site. Thus, P is the probability that the initial octahedral muon has an empty nearest neighbor tetrahedral site. This expression is chosen because the number of vacancies in the hydrogen lattice goes as $(1-x/2)$, and there are eight nearest neighbor tetrahedral sites for every available octahedral site. Λ^2_{EXP} for each sample is plotted as a function of $(1-x/2)$ in figure 2. The line is the least squares fit to equation (2) with Λ_{OCT} and Λ_{TET} the free parameters. The values determined from the fit are Λ_{OCT}=0.252(3) μsec^{-1} and Λ_{TET}=0.172(5) μsec^{-1}. This Λ_{TET} is discussed in section 3.3. The value for the octahedral site is lower than that calculated from the Van Vleck formula. Thus we conclude that the hydrogen lattice around the muon is displaced outward. We calculate that the nearest neighbor expansion is approximately 7% or that each hydrogen is displaced 0.15 Å outward. This distortion presumably arises from the shortness of the interstitial muon-hydrogen distance in an undistorted lattice ($\sqrt{3}/2$ times the hydrogen-hydrogen spacing), and the fact that the muon's spatial wavefunction is much larger than that of a hydrogen atom.

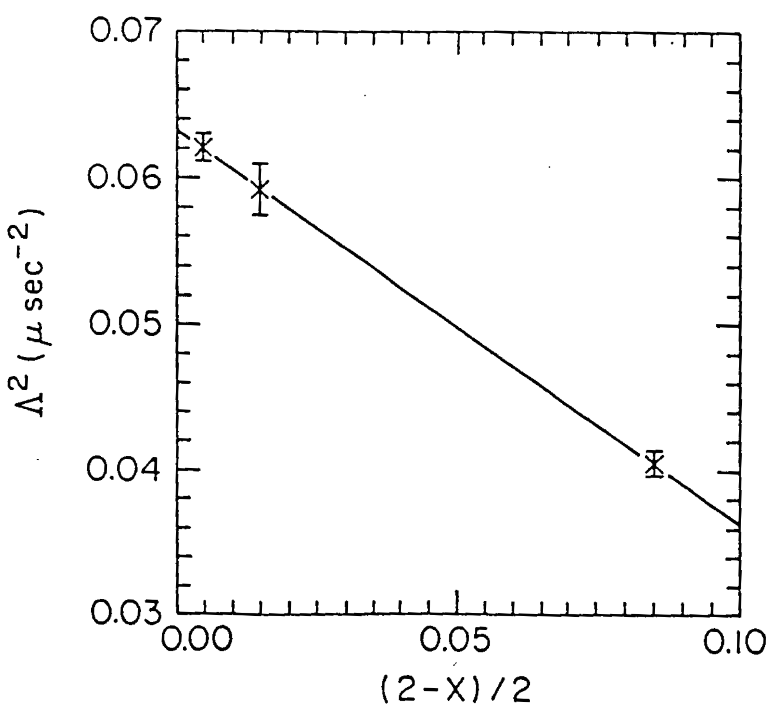

Fig.2. The depolarization parameter squared, Λ^2_{EXP}, in region I for each sample plotted as a function of fractional vacancy concentration. The line is a least squares fit to equation (2).

3.2. Region II

Figure 1 shows that the onset of motional narrowing for the various concentrations occurs at different temperatures below room temperature. Doyama et al. /2/ see the same type of behavior for $ZrH_{1.99}$ just above 300 K. Presumably their other ε phase sample (x=1.90) would exhibit this transition at lower temperatures than they report. This behavior may be explained qualitatively in the following way. For x=1.83 in region I, the muon stops in the tetrahedral site roughly 70% of the time. In region II the remaining 30% move to vacant tetrahedral sites. The fact that this motion occurs at low temperature might be explained by assuming an attractive force between muons and nearby vacancies. For x=1.97, the muon stops in the tetrahedral sites roughly 10% of the time, which means that 90% must find or be found by vacant tetrahedral sites. One would expect this to be difficult because only 3 out of 200 sites are vacant. For x=1.99 the picture is similar except that only 0.5% of the tetrahedral sites are vacant. For this sample in the temperature regime near 300 K the octahedral muons apparently move sufficiently rapidly to cause motional narrowing. Only at higher temperatures (above 350 K) is there evidence for increased tetrahedral trapping. Among other factors to be considered it may be that the activation out of the octahedral site may be associated with the transition from the δ to the γ phase since the change of c/a is over a range from 200 K to 310 K /6/.

3.3. Region III

Near room temperature figure I shows a concentration-independent plateau for x=1.83 and 1.97 and suggests that the same would be observed for x=1.99 if the measurements were extended to higher temperatures. The value for the depolarization rate of this plateau is 0.1764(16) μsec^{-1} which does agree with the value found in section 3.1, confirming our model for the low temperature region. This value however does not agree with that calculated from the Van Vleck formula for tetrahedral site occupancy. This concentration independence rules out the possibility that the muon is in a tetrahedral site with a nearest neighbor vacancy since one would expect the probability of a nearest neighbor vacancy to be low for x=1.97. The only other reasonable alternative is to assume that the muon is in a tetrahedral site and is distorting the local lattice. If this is the case, then one needs a nearest neighbor relaxation of 3% or 0.07 Å.

The tetrahedral site spacing in $TiH_{1.99}$ and $TiD_{1.98}$ are 2.227 and 2.220 Å respectively /6/ and we have found a 2.297 Å spacing for the muon-nearest neighbor hydrogen distance. If we assume these spacings are proportional to a constant plus a term proportional to the zero point motion ($\sim 1/\sqrt{m}$) we predict a 2.275 Å μ-H_{NN} spacing. The excess of our measured spacing over the predicted spacing observed presumably arises from there only being one muon in the sample at a time. The restoring forces that would arise if there were a lattice of muons are not present.

3.4. Region IV

Figure 1 shows a second region of motional narrowing. This is associated with the activation of hydrogen from tetrahedral sites.

Figure 3 presents the muon correlation times for two samples plotted as a function of 1/T. The features of this figure are: (i) the correlation times for protons and muons are of the same order and (ii) the activation energies for the muon (0.38 eV) and for the proton (0.507 eV /7/) are quite different. The first result is not surprising from the standpoint of classic blocking theory which predicts that motion of the lighter particle (muon) would be governed by the motion of the heavier particle (hydrogen) for systems where the hydrogen concentration is too high for percolation. However, the second result does not agree with a simple blocking theory implying

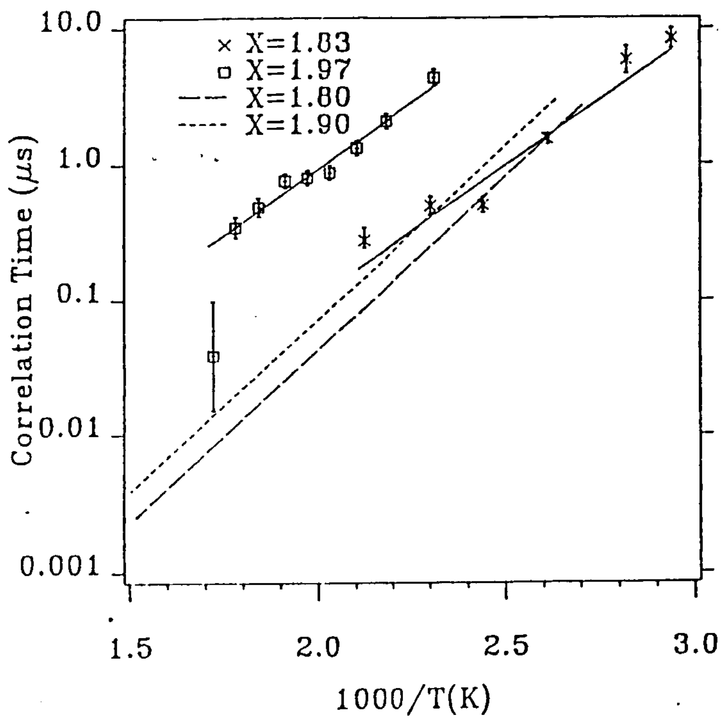

Fig.3. The muon correlation times plotted as a function of 1/T for $TiH_{1.83}$ and $TiH_{1.97}$. The proton correlation times for $TiH_{1.80}$ and $TiH_{1.90}$ obtained from T_1 measurements /7/.

that the muon's jump frequency is on the order of or less than that of hydrogen. Richter et al. /1/ have proposed an explanation for muons in metal hydrides. They observed that correlation times in μSR are a combination of muon and hydrogen jump rates and can be roughly approximated by:

$$\tau_c \sim \frac{1}{\Gamma_\mu(1-c)} + \frac{1}{\Gamma_H(1-c)}\ \frac{1-f}{f} \qquad (4)$$

yielding an order of magnitude result. Γ_μ and Γ_H are the muon and hydrogen jump rates. The correlation factor f, which is concentration dependent, takes into consideration all correlations beyond mean-field blocking for tracer diffusion. The factor (1-c) is the fractional number of vacancies and is equal to (1-x/2). If one uses the values obtained for τ_c by employing fits to the Abragamian form, the observed proton jump rate $36\times10^6 \exp(-.507eV/kT)\ \mu sec^{-1}$ /7/, and the values for f for each concentration /8/, then one obtains values for $\Gamma_\mu(T)$. If we assume an Arrhenius expression for $\Gamma_\mu(T)$:

$$\Gamma_\mu = \Gamma_{\mu o} \exp(-E_{a\mu}/kT), \tag{5}$$

we obtain $E_{a\mu}$=0.37(3) and 0.35(3) eV for x=1.83 and 1.97 respectively, and $\Gamma_{\mu o}=4\times10^5$ μsec^{-1} for both concentrations. From these results it appears that the muon jump rate is lower than that of hydrogen by approximately two orders of magnitude. The answer to this puzzlement may be connected with the assertion in region III that there is a 3% NN hydrogen lattice expansion for muon tetrahedral site occupancy. When the muon jumps from one tetrahedral site to another, it must also distort the lattice in its new site. For a tetrahedral site, the NN are four titanium atoms which are much more massive than hydrogen atoms and therefore require more energy to displace them. Thus, one may have a large reduction of the small polaron hopping integral. This could lead to a muon hopping rate much smaller than that of hydrogen. In this circumstance the correlation time of equation (4) is dominated by the first term, and the observed activation energy is that for the muon. The muon's activation energy might well be associated with the energy difference between the muon ground state and a barrier height. Since the muon's zero point energy is three times higher than that of a proton this could account for the lower E_a.

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